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Determination of the Exciton Binding Energy in CdSe Quantum Dots

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Abstract

The exciton binding energy (EBE) in CdSe quantum dots (QDs) has been determined using x-ray spectroscopy. Using x-ray absorption and photoemission spectroscopy, the conduction band (CB) and valence band (VB) edge shifts as a function of particle size have been determined and combined to obtain the true band gap of the QDs (i.e. without and exciton). These values can be compared to the excitonic gap obtained using optical spectroscopy to determine the EBE. The experimental EBE results are compared with theoretical calculations on the EBE and show excellent agreement.

In the field of colloidal quantum dot (QD) materials, the effects of quantum confinement (QC) as a function of QD particle size represent some of the most widely studied QD phenomena. Included in these QC effects is the increase in exciton energy as the particle size is reduced below the

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bulk Bohr exciton radius giving rise to unique optical properties that are highly tunable with particle size.¹ In CdSe QD materials, tunable optical properties are exhibited by particles in the 100 Å diameter and below range, because the bulk Bohr exciton radius for CdSe is ~ 56 Å.² Recently, there has been some controversy regarding the scaling of the exciton binding energy (EBE) with particle size. Early models, such as those based on the particle-in-a-box (PIAB),³ were used to predict that the EBE scales as the inverse of the particle radius, R^{-1} , which simply represents the Coulomb interaction between the electron and hole. More sophisticated theories, however, have predicted a deviation in the scaling of the EBE with particle size. For instance, Franceschetti and Zunger⁴ have used the empirical pseudopotential method (EPM) to predict that the EBE actually has a sublinear scaling factor, $R^{-0.86}$, for CdSe QDs. The apparent failure of the PIAB method is related to a few factors that include the use of a size-independent dielectric constant and crude boundary conditions for the wavefunctions (i.e. an infinite potential well at QD surface) in the model. Despite the rich literature on the theoretical description of the EBE for CdSe QDs, there has been no experimental investigation of the EBE. Irrespective of the theoretical methods used to calculate the EBE in CdSe,^{4,5} it is evident that the size induced increase in the EBE is much larger than the thermal energy making a simple temperature dependent optical absorption study incapable of deriving this quantity. In this letter, we report on the determination of the EBE for CdSe QDs. We find that the scaling of the EBE with particle size is sublinear and is in close agreement with the values predicted using EPM theory.⁴

One possible explanation for the predominance of theoretical studies of the EBE can be attributed to the inherent difficulties associated with an experimental determination. Ultra-violet/visible absorption spectroscopy is a very common analytical tool used in the characterization of CdSe QDs as the lowest energy absorption feature (the first exciton) can yield information on the QD size, crystallinity, and size dispersion.⁶ In addition, multiple exciton states can be resolved at higher energy for high quality QDs.⁷ The overriding problem with these studies, however, is that the excitonic states dominate the optical properties and the true electronic bandgap (BG) remains unresolved (see Figure Figure 4B for a description of the difference between the optical and electronic

band gap). The most elementary description of the electronic BG exists as the energy difference between the highest occupied states (valence band, VB) and the lowest unoccupied states (conduction band, CB). This value is fundamentally different than the excitonic states, which can occur anywhere from a few to hundreds of millielectron volts below the CB minimum (15 meV for CdSe versus 1 eV for LiF).⁸ A means of obtaining the electronic BG independent of the excitonic energy is of utmost importance in determining the EBE.

X-ray spectroscopies provide ideal methods with which to elucidate the absolute electronic BG energy of CdSe QDs. We have previously shown that the unoccupied states (CB states), can be independently resolved with elemental specificity using X-ray absorption spectroscopy (XAS).⁹ For CdSe QDs, the CB minimum shifts to higher energy with decreasing particle size in accordance with quantum confinement theories. In this manuscript, the filled states (VB states) are directly probed using valence band photoemission spectroscopy (VB PES). With VB PES, measurement of the ionization energies and energy profile of photoelectrons emitted from the VB yields the occupied VB DOS and enables an assignment of the energy of the VB maximum. One can, therefore, obtain the electronic BG by combining the energies of the VB maximum and CB minimum determined experimentally using VB PES and XAS. Subsequent comparison of the electronic BG with the excitonic gap obtained from optical absorption measurements will yield the EBE.

Results and Discussion

Figure 1 plots valence band photoemission (VB PES) spectra of different sized CdSe QDs and the corresponding bulk spectrum all excited at 90 eV. The bulk CdSe VB PES, shown in Figure Figure 1c, maps out the occupied DOS which consist of Se 4*p* orbitals at the top of the VB with the Cd 4*d* orbitals \sim 11 eV below the VB maximum. Although soft x-ray fluorescence (SXF) spectroscopy can be used to provide information on the VB DOS, for edges like the Se L₃ edge, the main decay channels occur through the core levels, obscuring any valence band features. SXF measurements were also attempted at the Se M_{2,3} edge as the Heske group has observed the upper valence band

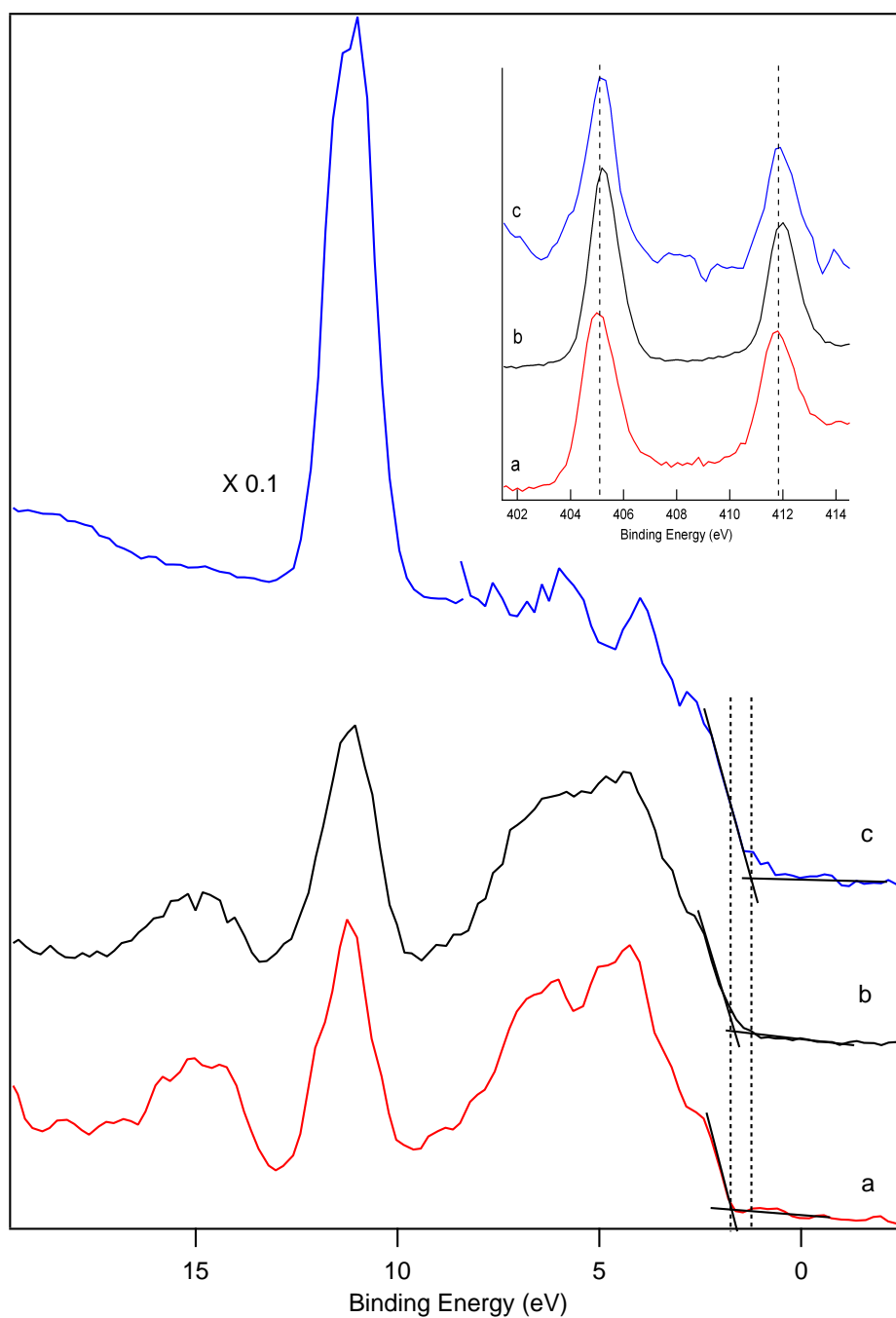


Figure 1: Valence band photoemission spectra of (a) 15 and (b) 19 Å radius CdSe QDs and (c) bulk CdSe(0001) wafer. Inset: Cd 3d_{5/2} and 3d_{3/2} core level PES spectra of the same size samples.

levels in CdS materials using S L_3 XES.^{10,11} In our experiments, however, we were only able to observe the core levels and not the valence band levels, with our measurements resembling previous work performed on spinels using Se $M_{2,3}$ SXF.¹²

The observed integrated intensity ratios between the Cd $4d$ and Se $4p$ (VB), I_{4d}^{Cd}/I_{VB}^{Se} , is $\sim 20:1$, which is consistent with both the atomic photoionization cross sections at 90 eV¹³ and previous VBPES measurements on bulk CdSe.^{14,15} To determine this ratio, the respective peaks were fit to Gaussian lineshapes. The Se component of the VB is modelled as a symmetric Gaussian lineshape with the "notch" considered to be the "peak" of the spectrum. Although the QD VBPES show similar features, an additional contribution to the DOS is observed between 5-7 eV that is attributed to carbon related features (capping molecules). Gentle heating of the NC samples, a practice known to remove some of the organic surfactant, leads to a decrease in the spectral intensity between 5-7 eV, which supports the assignment of these features to contributions from carbonaceous materials. We note that even high temperatures did not result in the complete reduction of the carbon features, thereby demonstrating that some amount of pyridine capping agent is chemisorbed to the particle at all times.¹⁶ In addition, the introduction of other capping groups with less carbon than pyridine, i.e. TGA (spectrum not shown), does not yield a reduction in the DOS features between 5-7 eV. We believe this arises from the fact that the sulfur moiety of the TGA is more tightly bound to the CdSe particle than the nitrogen atom of the pyridine. This, in turn, results in a larger carbon "signal" in the VBPES and helps us to assign the features to carbon.

The inability to remove all carbon contributions from the VBPES spectra induces some level of error into determining the absolute energy of the VB edge for a CdSe QD. Nonetheless, analysis of the intensity ratios between the Cd $4d$ and Se $4p$ indicate that the VB edge can be described in terms of the CdSe QDs and not of the carbon features on the surface of the particle. The obtained ratio, I_{4d}^{Cd}/I_{VB}^{Se} , for the QDs is $\sim 5:1$, which is a factor of four lower than observed in the bulk CdSe sample. The lower ratio can be explained by considering that the CdSe surface contains an excess of Se atoms. A recent study¹⁷ has proposed that CdSe QD surfaces have nearly a 50% excess of Se which could explain the differences in the ratio for our samples. As this experiment is based

upon the detection of ≤ 90 eV kinetic energy electrons that have a mean free path of up to ~ 1 nm, we are preferentially probing the QD surfaces and should be extremely sensitive to local changes in stoichiometry.

Figure 2 plots the observed VB shifts for CdSe QD samples with two different surface terminations, pyridine and TGA. The values for both the valence and conduction bands shifts are listed in Table 1. For energy calibration purposes, all the spectra were referenced to Cd 3*d* core level

Table 1: Experimental valence and conduction band shifts relative to the bulk values. The CdSe radius is measured in Å, ΔE_{VB} is the difference between the QD and bulk VB edge and ΔE_{CB} is the difference between the QD and bulk CB edge (both in eV)

| CdSe particle radius | ΔE_{VB} | ΔE_{CB} |
|----------------------|-----------------|-----------------|
| 19 | 0.16 | 0.65 |
| 15 | 0.66 | 0.65 |
| 14 | 0.77 | 0.72 |
| 6.25 | 2.04 | 1.20 |

PES spectra that were, in turn, calibrated versus Au 4*f* core level spectra from the underlying substrate. The Au offers an optimal means of calibration because the energy of the Au 4*f* orbitals are well characterized and the Fermi levels of the QDs and the substrate are aligned.¹⁸ Interestingly, and in contrast to previous reports,^{19,20} we do not observe a shift in the Cd 3*d* core levels. This result, although somewhat surprising, is reproducible over long time scans and multiple sample preparations. Moreover, our results are similar to early studies on CdSe QDs where shifts of less than 0.1 eV (i.e. less than the experimental resolution) were observed.²¹ We have great confidence in the validity of the results presented in this letter for several reasons: (a) Comparison of the Cd 4*d* levels with respect to the Se 4*p* dominated VBM (Figure Figure 1) indicates that we are truly studying the QDs. In Ref. 19 and 20, the authors fail to discuss the Cd 4*d* levels in their analysis of the CdSe VB. Examination of the intensity profiles of the Cd 4*d* levels and the VBM is essential to ensure that one is truly studying the VB of the CdSe material, and not spurious carbon or impurities which may have a stronger VB photoemission cross section. (b) Plots of both the Cd 3*d*_{5/2} and 3*d*_{3/2} provide no evidence for sample oxidation (inset of Figure 1). (c) Multiple spectra recorded on both identical and distinct regions of each sample show little variation in the CdSe peak position ($2\sigma < 0.05$ eV). This indicates that sample charging plays no role in our experiments. (d) Our

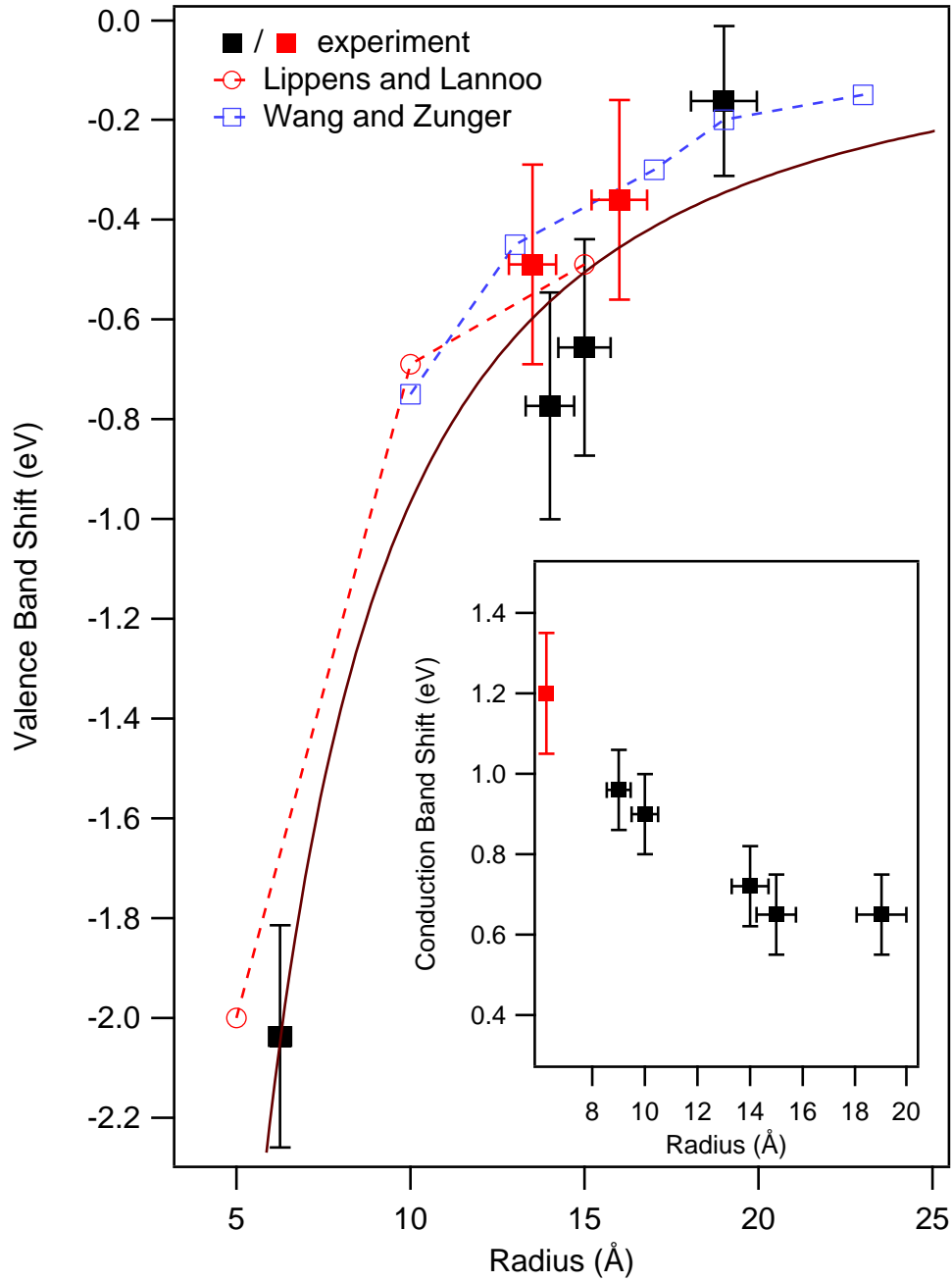


Figure 2: Size dependent values for CdSe QD valence band states. The and represents the pyridine and TGA data points, respectively, while the \circ (Ref. 24) and (Ref. 25) represent theoretical values. The lines for the theoretical points are guides for the eye, while the lines through the experimental points represents a least squares fitting of the data. Inset: Size dependent values for CdSe-TOPO QD conduction band shifts (Ref. 9).

reference spectra were recorded for a clean CdSe(0001) wafer. Using a well ordered crystal allows us to directly compare our results to published data,^{14,15,22,23} and to perform gentle heating of the wafer to drive off physisorbed organic contaminants. We attempted similar experiments on a CdSe powder and were unable to obtain a clean CdSe VB spectrum. In Refs. 19 and 20, the authors use CdSe powder as a reference rather than a CdSe crystal. Each of these factors provides strong support for the accuracy of our measurements and the associated discussion presented in this letter. Furthermore, they allow us to conclude that the shifts observed in our data can be described in terms of quantum confinement induced changes in the VBM, as opposed to core level / Fermi level shifting.

For the purposes of comparison, theoretical values^{24,25} for the VB shifts have been plotted alongside the experimental data. There is excellent agreement between experiment and theory, with the majority of the experimental values residing within experimental error of the theoretical values. In fact, the agreement between experiment and theory is far superior to the equivalent comparison reported in our XAS characterization of the CBM.⁹ In addition, we observe similar VB edge shifts for different surface terminations suggesting that the capping molecules does not affect the VB edge energy to any significant degree. The lack of surface sensitivity on the edge shifts is consistent with optical measurements.²⁶ For comparisons sake, the scaling laws associated with the VB and CB levels are,

$$E_{VB} = E_{VB}^{bulk} - \frac{38}{R^{1.6}} \quad (1)$$

$$E_{CB} = E_{CB}^{bulk} + \frac{4}{R^{0.6}} \quad (2)$$

where the numerator for the second term for both equations are in units of eV Å. For a more complete picture of the CdSe QD electronic structure, the experimental band gaps as a function of particle radius are plotted in Figure 3. The photoemission PE band gap is defined as the addition of the CB shift and VB shift to the bulk CdSe value,

$$E_{BG}^{PE} = E_{CB} + E_{VB} + E_{bulk}^{CdSe} \quad (3)$$

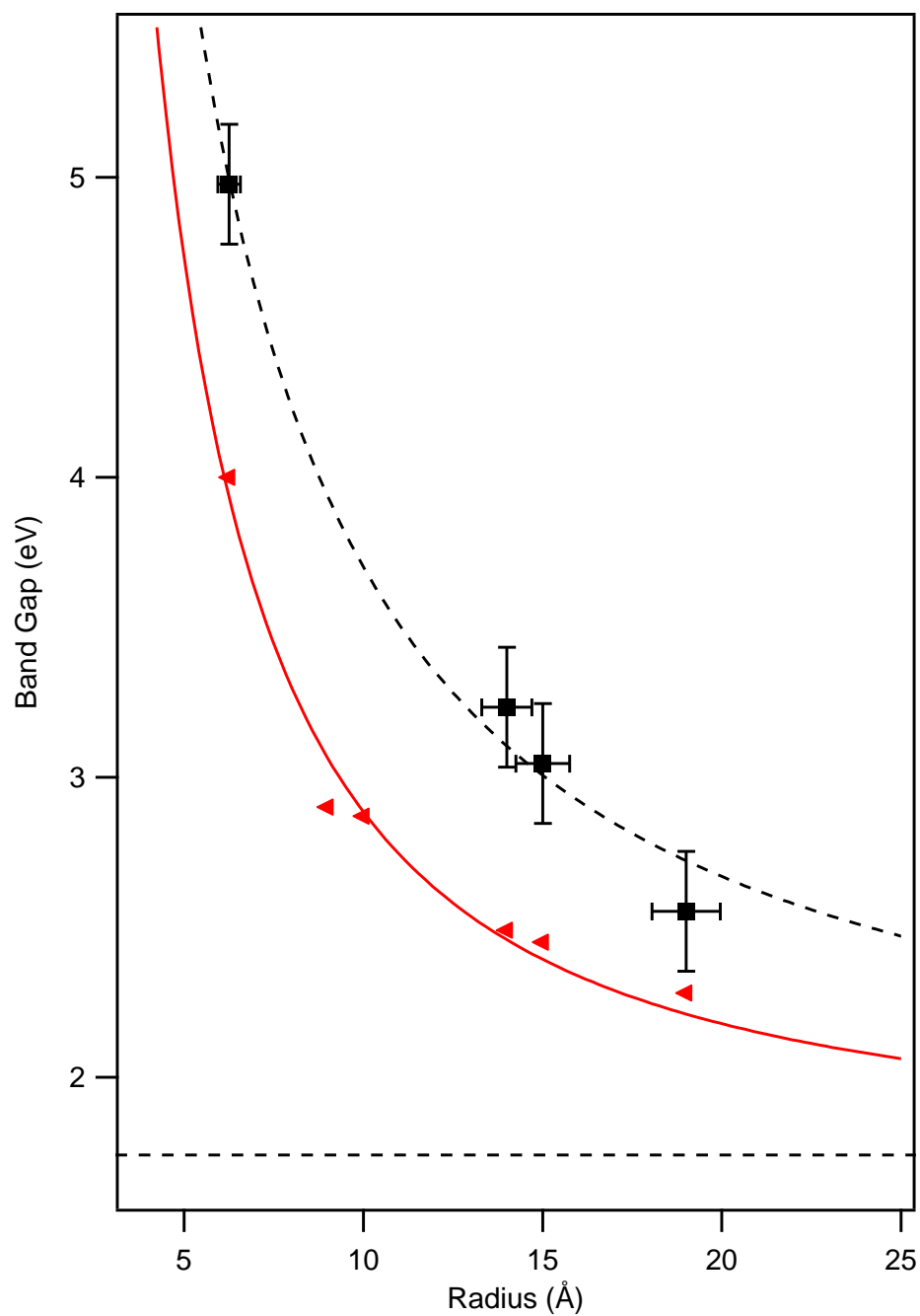


Figure 3: Band gap of CdSe QDs as a function of particle radius. The \blacktriangle represents the CdSe QD photoemission band gaps, the \blacksquare represents the CdSe optical absorption excitonic gaps.

, where $E_{bulk}^{CdSe} = 1.74$ eV (at 300 K).⁸ The PE gap () is plotted alongside the optical absorption (OA) excitonic gap () for purposes of direct comparison. Both the PE and OA gaps show a similar scaling with size, $R^{-0.6}$ and $R^{-0.7}$, respectively.

Although the scaling for the two measurements are similar, an obvious offset is present between the two data sets. If one takes the difference between the two data sets and plots them as a function of size (Figure 4), it is evident that the difference increases with decreasing particle size. This difference is the EBE and the conceptual derivation of this value is illustrated in Figure 4B. Put simply, the EBE is the difference between the electronic band gap (from PES) and the excitonic gap (from optical absorption). Remarkably, the overlap between our experiment and theory is excellent. The scaling law associated with the experimental EBE can be written as $EBE \sim 1/R^n$, where $n = 0.72$. Franceschetti and Zunger⁴ have shown theoretically that $n = 0.86$ for CdSe QDs using the empirical pseudopotential method (EPM). Both experiment and EPM theory predict that the EBE scales *sublinearly* with particle size, in contrast to the PIAB model which predict the EBE scales inversely proportional with particle size (Coulomb energy).

One factor that is neglected in this discussion is the contribution of the *core* exciton binding energy (CEBE). It has been previously reported that the size dependent increase in the CEBE in CdS QDs led to strong features in the S L_3 absorption edge and made straightforward analysis of the edge onset difficult.²⁷ As a consequence, an important question arises for CdSe QDs: must the CEBE be considered in this analysis? To answer this question, one must consider the strength of the CEBE in the bulk material and how a reduction in particle size may affect the value. Following Carson et al,²⁸ the CEBE can be described by,

$$E_{CEBE} = R_H \left(\frac{\mu}{\epsilon^2} \right) \quad (4)$$

, where R_H is an atomic Rydberg constant, μ is the reduced mass, and ϵ is the dielectric constant. Using Eq. 2, the values of E_{CEBE} are ~ 10 and 100 meV for bulk CdSe and CdS, respectively. Without knowing the exact effect that quantum confinement has on the CEBE, we need to make an

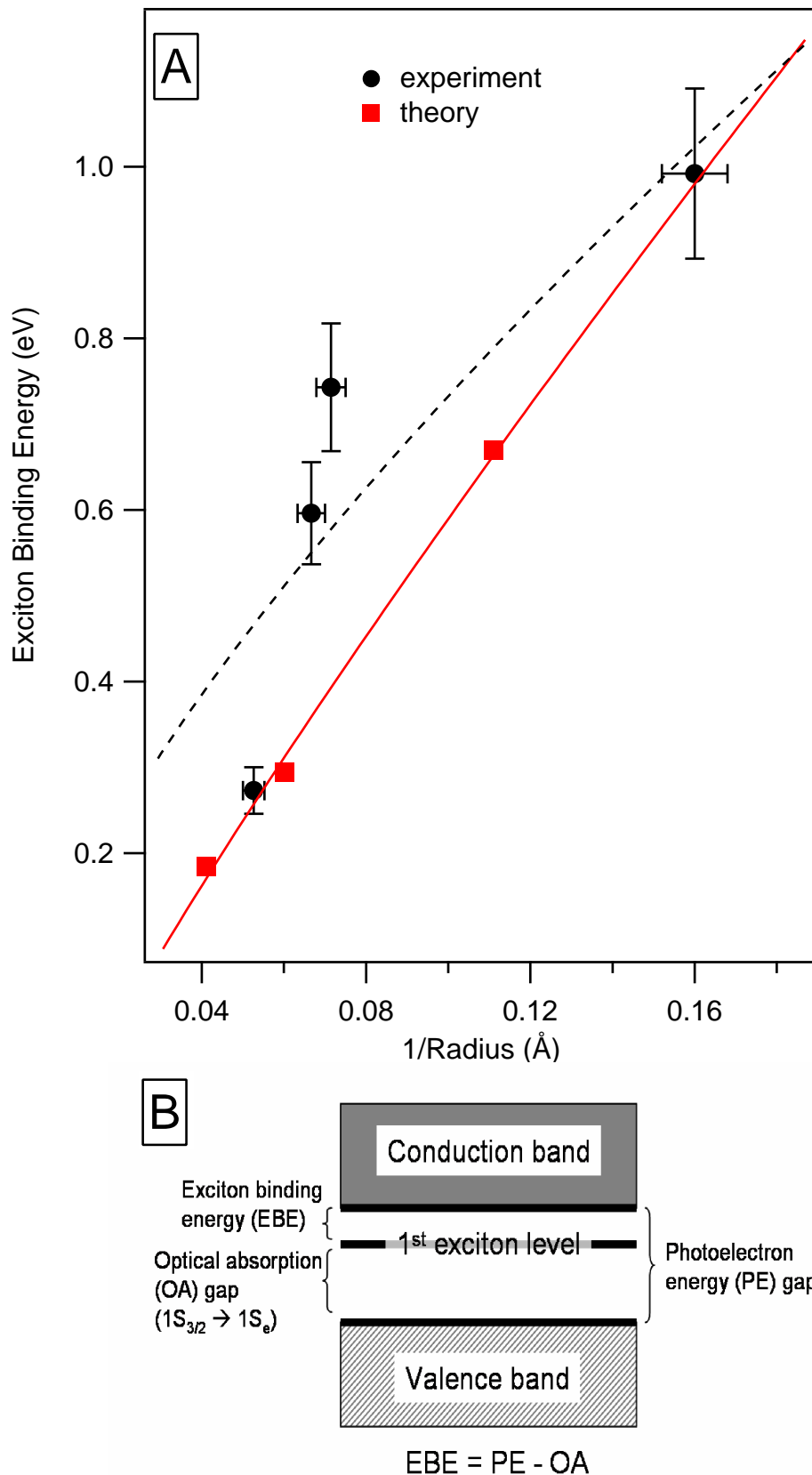


Figure 4: (A) Exciton binding energy of CdSe QDs as a function of particle radius. The ● represents the CdSe-TOPO QD experimental exciton binding energy while the ■ represents the theoretical values (Ref. 4). (B) Illustration of energy bands depicting the definition of the exciton binding energy, optical absorption gap, and photoelectron band gap.

assumption on the scaling of the CEBE with particle size. If we consider that the CEBE increases by an order of magnitude (i.e. a large increase) at small particle sizes, we can estimate that the CEBE increases to 100 and 1000 meV for CdSe and CdS, respectively. When we consider that the values that we obtained for the EBE were on the order of 1 eV for small particles of CdSe, the exclusion of the CEBE provides an upper range of the error of this value ($\sim 10\%$). In the case of CdS QDs, the size induced increase of the CEBE may rival the value of the EBE and it is understandable why the CEBE could not be ignored in Ref. 27. In the case of CdSe, however, the CEBE is on the order of typical experimental error and can be neglected in this current analysis.

Conclusions

In conclusion, we have obtained the EBE of CdSe QDs using x-ray spectroscopy. The EBE is size dependent and can reach values of nearly 1 eV at the smallest particle sizes studied. The experimental EBE values were compared to those obtained by EPM theory and a strong agreement is observed. These results illustrate that x-ray spectroscopy is a valuable tool to observe new physics that it is not possible to address with more conventional methods.

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Methods

Synthesis of CdSe quantum dots

CdSe QDs were produced by previously reported methods using precursors of cadmium oxide (CdO), dimethylcadmium ($\text{Cd}(\text{CH}_3)_2$), tetradecylphosphonic acid (TDPA), trioctylphosphine oxide (TOPO) and hexadecylamine(HDA).^{29,30} The QDs were then dispersed in toluene and then precipitated with methanol several times to remove unreacted precursors and residual capping ligands. Final dispersions of clean CdSe QDs were in hexane. In general, high quality core level PES data was obtained for QDs with this surface termination, but VB PES data of comparable quality was difficult to obtain.

Ligand exchange of CdSe quantum dots

To mitigate the problem observed with TDPA/TOPO/HDA coated QDs, we then studied QDs overcoated with pyridine or thioglycolic acid (TGA), which were prepared from the original CdSe samples via established ligand exchange techniques.²⁶ The ligand exchange was performed for two reasons: (a) to aid in reducing carbon related features in the VB which obscure the valence band edge features of the QDs and (b) to help reduce charging during the PES measurements. The TDPA/TOPO/HDA combination contains many carbon atoms (i.e. TOPO posses 24 carbon atoms), while pyridine and TGA contain 5 and 2 carbon atoms, respectively. Hence, the ligand exchange results in a substantial reduction in carbon content per capping molecule. The pyridine ligand is also labile in vacuum and, since the pressure in our PES chamber is $\leq 5 \times 10^{-9}$ Torr, we can anticipate that some of the pyridine will desorb, leading to a further reduction in the carbon (organic) features in the VB. Long alkyl chains, a feature of both TOPO and HDA, are insulating and can limit charge transfer from the QD to a surface, which can lead to sample charging.³¹ The use of an short aromatic chain, like pyridine, facilitates charge transfer and reduces any charging effects. The general features in the PES spectra of the three different sample sets are extremely similar, with the main differences apparent in the VB region.

Valence band and core level photoemission measurements of CdSe quantum dots

Valence band and core level PES measurements were performed at beamline 8-2 at the Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center. The CdSe QDs samples were deposited onto Si(111) wafers from hexane. To ensure integrity of the samples, we employed a few protocols. First, different samples were measured from different synthetic preparations. Second, spectra were recorded before and after exposure to the intense x-ray beam to look for any beam damage or charging effects. Third, a consistent method to preparing our films was employed. A small amount (1mg) of QD samples was dissolved in ~ 1 mL of solvent. With an Eppendorf, amounts on the order of 10 μ L were added dropwise to the Si substrate and repeated to ensure a thick enough film would be formed (to eliminate contributions from Si valence band features). QD samples were also prepared in an identical manner on Au coated Si(111) for the purposes of core level calibration studies using PES. The photoelectrons were detected with a cylindrical mirror analyzer with a pass energy of 25 eV which provides an experimental energy resolution of ~ 0.2 eV. All the VBPES spectra were recorded at an excitation energy, E_{ex} , of 90 eV, while the core level PES spectra were collected using $E_{ex} = 530$ eV unless otherwise noted.

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